

Origin of Giant Optical Nonlinearity in Charge-Transfer–Mott Insulators: A New Paradigm for Nonlinear Optics

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Neither pure Mott insulators nor pure charge-transfer insulators have ever been considered as a possible candidate for nonlinear optical (NLO) materials since individually neither the strong correlation (U) nor the large charge transfer (Δ) is favorable to the NLO response. However, in their composites, charge-transfer–Mott insulators, jointly Δ and U can enhance the hyperpolarizability (γ) by guiding the ground states into the antiferromagnetic phase and the excited states into the charge-transfer phase. These Δ and U that maximize γ form a unique golden Δ - U line, on which the recently observed giant nonlinear optical effect is just a single point, whose physical origin is that the system is driven into a phase-separated region for the ground and excited states. This novel mechanism may suggest a conceptually new paradigm to explore an even larger optical nonlinearity.

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Materials exhibiting a large optical nonlinearity are rather unique, whose selections are often involved partly because not only the ground state but also the excited states matter [1,2]. Two common wisdoms have been that the material should have (a) a larger charge delocality and (b) a lower dimensionality (quantum confinement). Metals and superconductors do have a large charge delocalization but their strong optical absorption and screening effects make them unsuitable; regular insulators are not proper either since they lack a charge delocality and a strong oscillator strength. Thus, to this end, one has never expected that Mott insulators (MTI) and charge-transfer insulators (CTI) can be utilized as a nonlinear optical (NLO) material. However, this old paradigm is now challenged by the newly found giant nonlinear optical effect (GNLO) [3] in one of nickel halides ($[\text{Ni}(\text{chxn})_2\text{X}]_2$, or Ni-X, where chxn refers to cyclohexanediamine and X is Br or Cl). The observed GNLO, with at least 2 orders of magnitude enhancement, is rather specific to Ni-Br though other compounds have a similar structure. Up to now, its physical origin has been unclear.

In this Letter, we will demonstrate that a novel mechanism underlies GNLO in the charge-transfer Mott insulators (CTMI). Although individually the electron correlation and the charge transfer are unfavorable to the NLO, coming together they can maximize the hyperpolarizability by driving the ground state into the antiferromagnetic phase and the excited states into the charge-transfer phase. This requires a delicate balance between the charge transfer and the electron correlation. As a consequence, we identify a unique Δ - U line on which the recently observed giant nonlinear optical effect is just a single point. This may suggest a conceptually new paradigm to increase the nonlinear optical responses.

Ni halide has a well-defined one-dimensional structure, $\cdots\text{—Ni—X}^-\text{—Ni—X}^-\text{—Ni—X}^-\text{—}\cdots$, whose electrons dominantly move along the chain direction. One unpaired d_{z^2} orbital on nickel ions is hybridized with

one p_z orbital from halides. The centers of d and p bands can be shifted with respect to each other by the charge-transfer energy Δ which can be tuned by choosing different halides. Ni ions have a larger on-site repulsion U_{Ni} than U_X of halides. As is well known, the whole system can be described by a two-band Hamiltonian [4],

$$H = -t \sum_{i,\sigma} (\hat{d}_{i\sigma}^\dagger \hat{p}_{i+1\sigma} + \hat{p}_{i+1\sigma}^\dagger \hat{d}_{i\sigma}) + \Delta \sum_{i,\sigma} (-1)^i \hat{n}_{i\sigma}^{d(p)} + \sum_i U_{\text{Ni}(X)} \hat{n}_{i\uparrow}^{d(p)} \hat{n}_{i\downarrow}^{d(p)} + V \sum_{i,\sigma,\sigma'} \hat{n}_{i\sigma}^d \hat{n}_{i+1\sigma'}^p, \quad (1)$$

where $\hat{d}_{i\sigma}^\dagger$ ($\hat{p}_{i\sigma}^\dagger$) is the d (p) electron creation operator with spin $\sigma = (\uparrow, \downarrow)$; $\hat{n}_{i\sigma}^{d(p)} = \hat{d}_{i\sigma}^\dagger \hat{d}_{i\sigma}$ ($\hat{p}_{i\sigma}^\dagger \hat{p}_{i\sigma}$); t is the hopping integral between d and p orbitals and is chosen as the energy unit ($t = 1$); V is the interatomic correlation. According to the experimental estimations [5,6], we assume that U_X is 1 and $V = 0.8$. Other parameters will be specified later. The current operator is defined as usual $\hat{J} = -iet \sum_{i,\sigma} (\hat{d}_{i\sigma}^\dagger \hat{p}_{i+1\sigma} - \hat{p}_{i+1\sigma}^\dagger \hat{d}_{i\sigma})$, where e is the electron charge. The ground and excited states are computed by the exact diagonalization scheme. The nonlinear optical response is then calculated by a standard scheme [7].

The microscopic nonlinear optical response is derived from the interaction between a medium and the radiation field. This interaction distorts the electron cloud and generates an induced dipole moment μ_{ind} in the medium which can be expanded in the electric field \mathbf{E} of light as [8], $\mu_{\text{ind}} = \alpha \mathbf{E} + \beta : \mathbf{E} \mathbf{E} + \gamma : \mathbf{E} \mathbf{E} \mathbf{E} + \dots$. Here the quantity α is the linear polarizability, which describes the linear optical response to the applied field. The coefficients β and γ describe, respectively, microscopic second- and third-order nonlinear optical responses, and are called the first and second hyperpolarizabilities. Our interested hyperpolarizability γ thus quantifies the third-order nonlinear response of the medium. In Fig. 1, we plot the maximal

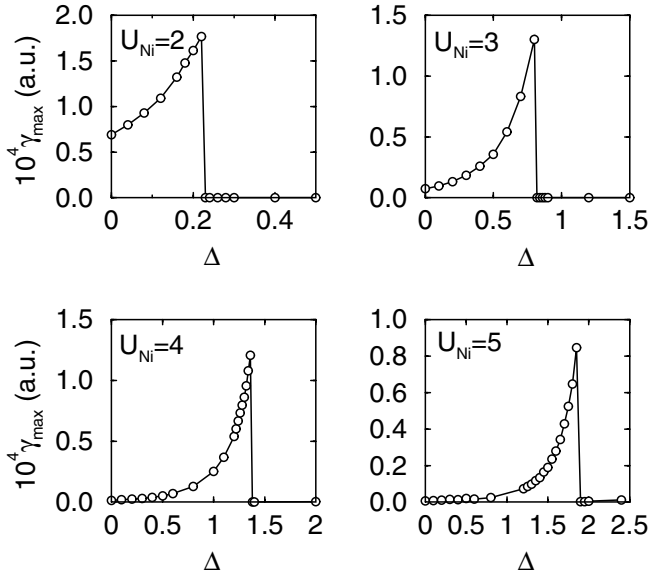


FIG. 1. Maximal hyperpolarizability γ_{\max} as a function of charge transfer Δ for $U_{\text{Ni}} = 2, 3, 4, 5$ with $U_X = 1$.

hyperpolarizability γ_{\max} (as measured experimentally [3]) versus the charge transfer Δ for four different sets of parameters at system size $N = 8$ [9] with a periodic boundary condition. To begin with, let's focus on the case with $\Delta = 0$, in the absence of charge transfer. One notices that with an increase in U_{Ni} from 2 to 5, γ_{\max} is reduced more than 2 orders of magnitude. This is understandable even for the linear optical response in a simple Hubbard model, where the optical conductivity $\sigma(\omega)$ obeys the f -sum rule [10], $\int_0^\infty d\omega \sigma(\omega) = -\langle T \rangle / 2N$. And the kinetic energy $\langle T \rangle$ depends on U as

$$-\langle T \rangle / 4Nt \sim (1 - 0.21358U^2/16)/\pi, \quad \text{for } U \ll 1; \quad (2)$$

$$\sim \left[\frac{1}{8} \ln 2 - \left(\frac{3}{64} \right)^2 \zeta(3) U^{-2} \right] U^{-1}, \quad \text{for a large } U. \quad (3)$$

Since $\langle T \rangle$ is reduced upon increase in U , the optical response is suppressed. This is the basic reason why the common Mott insulators without charge transfer are not suitable for NLO. However, with a nonzero Δ , we see a different picture. For $U_{\text{Ni}} = 2$ and $U_X = 1$ (see Fig. 1), we notice a sharp increase in γ_{\max} with Δ up to $\Delta_c = 0.22 \pm 0.002$; for other sets of parameters, we observe a similar dependence but their Δ_c 's are moved toward a high value. We will return to this point below. Now, at $\Delta = \Delta_c$, for different U_{Ni} their γ_{\max} 's become rather comparable though as expected, γ_{\max} is still reduced with U_{Ni} but only about 2 times reduction in their magnitudes, rather than 2 orders of magnitude change at $\Delta = 0$. This reveals a novel dimension in those Mott-charge-transfer insulators to achieve a large nonlinear optical response, and more importantly underlies a new paradigm as seen soon.

From Fig. 1, we notice a big drop of γ_{\max} after Δ_c , which serves as a good starting point to understanding the underlying physics. In the following, we compare two cases around this drop with $\Delta < \Delta_c$ and $\Delta > \Delta_c$ to see why the γ_{\max} is so different. In Figs. 2(a) and 2(b), we display the particle distributions $n(i) \equiv \langle \Psi | \hat{n}_i | \Psi \rangle$ versus site indices i (odd i 's denote Ni, even ones X) for two different parameters $\Delta = 0.22$ and 0.23 , where the circles and the boxes refer to the ground state and the dominant dipole-allowed excited state, respectively. $|\Psi\rangle$ is a wave function. The figure shows that for both cases, the ground states are similarly in their antiferromagnetic (AF) phases [11] with electrons piled up on the X atoms. Therefore, not surprisingly, we find that both wave functions have a big contribution from configurations like $|\phi_1\rangle = |\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\rangle$. On the other hand, a remarkable difference is observed in the excited states. For $\Delta = 0.22$, $n(i)$ is nearly a constant [Fig. 2(a)], meaning that there is a significant charge transfer in the excited state between Ni and X atoms with respect to the ground state, in good agreement with the experimental observations [5]. Since the excited state's wave function has large components like $|\phi_2\rangle = |\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\rangle$ and the current operator has the largest element $\langle \phi_2 | \hat{J} | \phi_1 \rangle$ between $|\phi_1\rangle$ and $|\phi_2\rangle$, the transition matrix element between the ground state and the excited state is maximized, which is the fundamental reason of the giant nonlinear optical response. We emphasize that such a desirable scenario is a result of the competition between the charge transfer and the electron correlation. A pure and large on-site correlation only leads to an antiferromagnetic phase. The charge transfer reverses the trend set by the correlation, which is already clear even in the dimer limit where U prefers a ground state of $|\uparrow\uparrow(\downarrow)\downarrow\rangle$

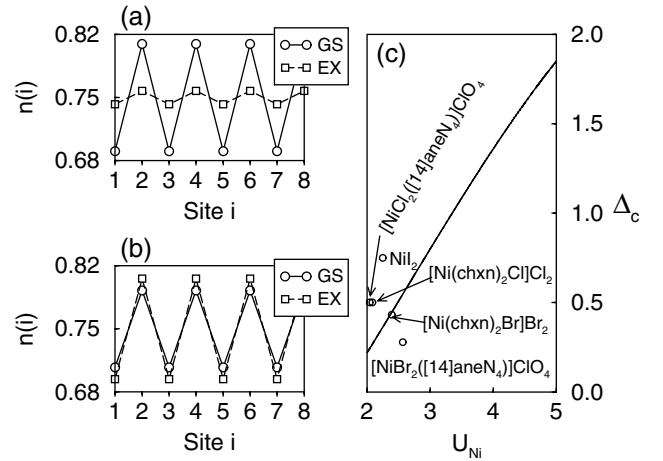


FIG. 2. On-site populations for the ground states and the excited states for (a) $\Delta \leq \Delta_c$ and (b) $\Delta > \Delta_c$. Configurations are similar for the ground states in (a) and (b) but are significantly different for the excited states. Here $U_{\text{Ni}} = 2$ and $U_X = 1$. (c) Golden (Δ - U) line. The small circles refer to different compounds as denoted by their chemical formulas, respectively. $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$ almost accurately sits on the line.

while Δ favors that of $|\uparrow\downarrow\uparrow\rangle$ ($|\downarrow\rangle$). Since the excited state is more sensitive to the variation of charge transfer, the charge transfer can almost solely alter the excited-state phase without affecting the ground-state phase strongly. This is extremely important because if both the excited states and the ground state shared the same phase, the transition matrix element would become very small.

On the other hand, we know that a too large charge transfer is also detrimental to NLO. Therefore, once we further increase Δ , say to 0.23, the excited state now has a similar charge distribution to that of the ground state, [see Fig. 2(b)]. This is because a too large Δ pins the charge fluctuation, effectively induces a “static dipole” and drives the wave function away from those ideal configurations (see above) to the configuration typically like $|\phi_3\rangle = |\downarrow\downarrow\uparrow\uparrow\downarrow\downarrow\rangle$, where we draw a box around two double-occupied sites and call them “domain walls.” These domain walls, once they prevail in the wave function, block the electron motion and reduce the transition matrix considerably. Therefore, whenever they appear, the hyperpolarizability becomes extremely small, which is the reason for the sharp reduction of γ after Δ_c . Coming back to Fig. 1, we now understand the role of charge transfer. Since a larger on-site interaction pins the antiferromagnetic phase stronger, the critical charge-transfer Δ_c required to “break” the phase naturally becomes larger. A delicate balance between U_{Ni} and Δ forms a unique “golden line,” which is displayed in Fig. 2(c). On this line, all the γ 's are maximal. The line, which can be fitted to $\Delta_c \propto 0.7(U_{\text{Ni}} - U_X)$ for $2 \leq U_{\text{Ni}} \leq 5$, represents an optimal condition to maximize the hyperpolarizability in these CMTI. Such a condition is expected since even in the dimer limit, there are competing terms like $2\Delta - (U_{\text{Ni}} - U_X)$, with $\Delta_c = 0.5(U_{\text{Ni}} - U_X)$. In a real system, this line is shifted to a slightly larger value. Physically, the golden line refers to a group of materials which behave basically like a charge-transfer insulator but have a large enough charge transfer. Therefore we call them the charge-transfer–Mott insulator.

Our theoretical prediction can be directly compared with the experimental results. In order to do so, we have to determine those parameters for a series of charge-transfer materials. Previous optical absorptions [5,6] and x-ray spectroscopy studies [12], together with our own fitting, give us a group of parameters for nickel-based CTMI as listed in Table I. In Fig. 2(c), these parameters (scaled with their hopping integrals) are compared with our theoretical curve. The figure shows that for different compounds, the parameters scatter rather widely (see small circles). However, we can identify one point that accurately sits on our golden line. This point corresponds to the compound $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$, which is in a remarkable agreement with the experiment finding [3]. The experiment [3] showed that only in $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$ has $\chi^{(3)}$ been enhanced more than 2 orders of magnitude but not in other compounds. Concerning some uncertainties in these pa-

TABLE I. Experimental parameters for five different Ni compounds.

	t (eV)	U_{Ni} (eV)	Δ (eV)
NiI_2	2.0 ^a	4.5 ^a	1.5 ^a
$[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$	2.3 ^b	5.5 ^b	0.993 ^c
$[\text{Ni}(\text{chxn})_2\text{Cl}]\text{Cl}_2$	2.4 ^b	4.9 ^b	1.2 ^b
$[\text{NiBr}_2([\text{14}] \text{aneN}_4)]\text{ClO}_4$	2.3 ^b	5.9 ^b	0.64 ^b
$[\text{NiCl}_2([\text{14}] \text{aneN}_4)]\text{ClO}_4$	2.4 ^b	5.0 ^b	1.2 ^b

^aRef. [12].

^bRef. [5].

^cThis work.

rameters, we consider this to be a strong experimental evidence supporting our theoretical results. Note that GNLO cannot be simply explained by either (1) the small energy gap since $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{I}_2](\text{ClO}_4)_4$ [13] has a similar small gap as $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$, or (2) the degeneracy [14] of the excited states since $[\text{Ni}(\text{chxn})_2\text{Cl}]\text{Cl}_2$ has a very similar degeneracy as $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$, or (3) the spin-charge separation [15] since Sr_2CuO_3 has a much larger electron interaction but exhibits a much smaller $\chi^{(3)}$ [3]. Hence, what makes $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_2$ unique is its charge transfer [12] which guides the system to the golden line and maximizes NLO effects. This may suggest a new direction for future experiments. In particular, the golden line maybe holds the key to an even larger optical nonlinearity. More importantly, the enhancement mechanism suggests a conceptually counterintuitive methodology to tailor the material's properties: both the charge transfer and the correlation are disadvantageous to the nonlinear optical response, but jointly they become advantageous to it. A pretty similar thing happens in the high T_c materials whose native materials are an insulator but once doped become a superconductor. Thus, we believe our study could have some impacts in other fields as well.

In conclusion, we have demonstrated that the giant optical nonlinearity is a consequence of the joint efforts of the charge transfer and the electron correlation. Although both the charge transfer and the electron correlation are unfavorable to the nonlinear optical response, together they can strongly enhance it by guiding the ground state into the antiferromagnetic phase and the excited states into the charge-transfer phases. These optimal electron correlations and charge transfers form a golden line, on which the recent experimental result is just a single point. Our work points out a new direction for future experiments and may suggest a conceptually new paradigm to explore an even larger optical nonlinearity.

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